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(54) OUTDOOR TITANIUM OR TITANIUM ALLOY MATERIAL EXCELLENT IN DISCOLORATION RESISTANCE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain outdoor titanium in which the generation of discoloration is prevented over a long period and free from the need of maintenance by imparting surface roughness i which the center line average roughness is prescribed and oxidized coating on the surface in which thickness is specified to outdoor titanium or the like.

SOLUTION: The surface roughness of an outdoor titanium or titanium allay material is regulated to ≤3 m, preferably to ≤1.5μm by the center line average roughness Ra, and the thickness of oxidized coatin on the surface is regulated to ≥20Å preferably, to ≥40Å. Furthermore, the regulation of the surface roughness is executed by regulating the surface roughness of rolling rolls, rolling loads and th velocity thereof, and for the regulation of the thickness of the oxidized coating, an oxidation treating method by heat treatment and an anodic oxidation treating method of forming oxidized coating by flowing electric current to titanium in a soln. are adopted. In this way, the outdoor titanium or titanium allay material excellent in discoloration resistance can be obtd.

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CLAIMS

[Claim(s)]
[Claim 1] Outdoor-type titanium or titanium-alloy material excellent in the color fastness characterized by for surface roughness being 3 micrometers or less in center line average-of-roughness-height Ra, and surface oxide-film thickness being 20A or more.
[Claim 2] Outdoor-type titanium according to claim 1 or titanium-alloy material said whose surface roughness is 1.5 micrometers or less in center line average granularity Ra.
[Claim 3] Outdoor-type titanium according to claim 1 or 2 or titanium-alloy material said whose oxide-film thickness is 40A or more.
[Claim 4] Outdoor-type titanium according to claim 1 to 3 or titanium-alloy material in which said oxide film is formed of oxidation treatment or anodizing by heating.

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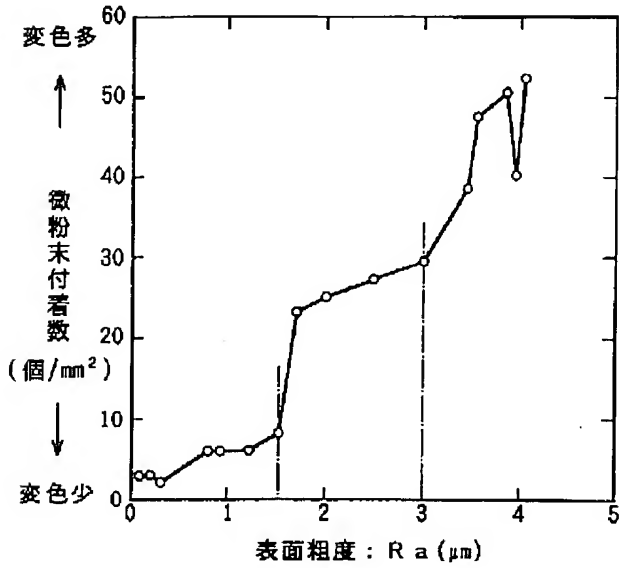
Drawing selection Representative drawing



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention is used for an outdoor-type way like a building sheathing material or monument material (for example, monument etc.). Although especially a fine sight poses a problem, when it is especially used for these applications about the titanium or the titanium-alloy material applied as a material Dirt with the passage of time can be controlled as much as possible, and it is related with the outdoor-type titanium or the titanium-alloy material (it may represent with "titanium material" below) which demonstrates the effectivene excellent in color fastness.
[0002]
[Description of the Prior Art] In recent years, by generating of acid rain, progress of waterfront development, etc by air pollution, the operating environment of building sheathing materials, such as roofing and outer wall mater or monument material is becoming severe, and the outstanding corrosion resistance is required of the metallic material used for an outdoor-type way. As a metallic material used for such an outdoor-type way, things made comparatively good [corrosion resistance], such as aluminum, stainless steel, and copper, have been used from former.
[0003] however, under the situation that an operating environment is becoming severe, with such a metallic material, it cannot say that it can fully respond but the use is increasing by recent years as what the titanium material which has the corrosion resistance which was markedly alike and was superior to the above-mentioned metallic material to acid rain or seawater replaces with the above-mentioned metallic material.
[0004] Although it will pass in about ten years since titanium material begins to be used for the above-mentioned application, the report that corrosion occurred until now is not made. However, the discoloration appropriate for brown a little may arise like metallic materials, such as aluminum used conventionally, stainless steel, and coppe as duration of service becomes long. although not necessarily fully solved an old place about the cause which suc discoloration generates, when such discoloration occurs, a fine sight will be spoiled, if a discoloration part is resembled to that extent and it depends.
[0005] Now, the actual condition has removed discoloration by carrying out polishing with the light front face by surface wiping by acids, such as nitric-hydrofluoric acid, or the abrasive paper for whenever [the / every], when cannot say that the technique of preventing generating of the above-mentioned discoloration is established since cause of dirt with the passage of time is not solved but discoloration occurs. However, there is a problem that maintenance nature is bad, with such a countermeasure. The actual condition is that continue at a long period of time, and such discoloration does not occur from such a thing, namely, extent which a maintenance free can attai is expected development of the outdoor-type titanium material excellent in color fastness.
[0006]
[Problem(s) to be Solved by the Invention] This invention is made under such a situation, it is a thing and the purpose is in offering the outdoor-type titanium or the titanium-alloy material which was excellent in extent whic can attain the maintenance free which continues at a long period of time and discoloration does not generate at color fastness.
[0007]
[Means for Solving the Problem] The outdoor-type titanium or the titanium-alloy material of this invention whic was able to attain the above-mentioned purpose has a summary at the point that surface roughness is 3 micromete or less in center line average-of-roughness-height Ra, and surface oxide film thickness is 20A or more.
[0008] In the above-mentioned outdoor-type titanium or titanium-alloy material, it is desirable that said surface

roughness is 1.5 micrometers or less in center line average-of-roughness-height Ra. Or as for said oxide film thickness, it is desirable that it is 40A or more.
[0009] In addition, the above-mentioned oxide film is mentioned as a means with effective oxidation treatment o anodizing by heating etc. as the means, although it can form with various means to mention later.
[0010]
[Embodiment of the Invention] Under the above-mentioned background, this invention persons inquired from various include angles aiming at development of titanium material with little dirt with the passage of time. And t cause of the dirt of titanium material with the passage of time was able to be clarified first. That is, according to t place which this invention persons examined, dirt with the passage of time showed clearly that two factors, following (a) and (b), are involving at least.
(a) Fe, C and NaCl which exist in atmospheric air, and SiO2 etc. -- growth (increment in thickness) of the oxide film of the titanium material front face by adhesion of gas constituents which exist in the physical (adhesion b) atmospheric air to the titanium material front face of a suspension component, such as SOx and NOx, moisture, e

[0011] That is, the fines of the rust which generates Fe under above (a) from iron sand, a structural steelwork, etc the component by which C is contained in exhaust gas from works etc., and NaCl are the sand to which the dropl and seawater component of seawater adhered, and SiO2. Discoloration arises by it being thought that it originate respectively, and these flying to the front face of titanium material, and adhering to sand physically.
[0012] On the other hand, gas constituents, such as SOx under above (b) and NOx, are components under smoke eliminating from an automobile or works, and moisture rains [moisture,] in atmospheric air. If these exist in the front face of titanium-alloy material, it will dissolve into moisture and SOx and NOx can do the sulfuric acid and nitric acid of super-low concentration. Although titanium is not macroscopically corroded at all from an acid of t level, and it is ultralow volume microscopically, the titanium on the front face of the maximum is eluted as ion. This eluted titanium ion reacts with the oxygen in atmospheric air, and moisture, and forms an oxide film. And th oxide film is visible to colored by the cross protection of light, if it will be in the condition of having involved in the above-mentioned gas constituents and this oxide film becomes the above thickness to some extent. moreover the process in which this oxide film is formed -- Fe of the above (a), C, NaCl, and SiO2 etc. -- if a suspension component is involved in into an oxide film, it will become what a thinner oxide film is [a thing] also visible to colored (that is, discoloration is promoted).
[0013] Then, when physical adhesion of the suspension component in (a) atmospheric air and generation of the oxide film of (b) titanium front face could be prevented effectively, this invention persons thought that the dirt of titanium-alloy material with the passage of time could be prevented or mitigated, and repeated research wholeheartedly about the concrete means.
[0014] Consequently, first, since the above (a) was physical adhesion of a suspension component particle, it considered the gestalt of a titanium material front face that what is necessary is just to change into the condition t a particle cannot adhere easily. Then, it investigated about the relation between the surface roughness of titanium material, and particle adhesion.
[0015] Drawing 1 is a graph which shows the surface roughness (center line average-of-roughness-height Ra) of titanium material, and the relation of particle adhesion (the number of impalpable powder adhesion). The titanium material adjusted to various surface roughness in this experiment, Fe, C and NaCl which were used as microscop powder, and SiO2 After putting in mixed powder in the chamber and agitating fines for 10 minutes with pneuma pressure, the sample front face was observed under the scan mold microscope (SEM), and the number of adhesio of the impalpable powder of per an unit area (mm2) was measured.
[0016] Surface roughness can mitigate adhesion of impalpable powder by center line average-of-roughness-heigh Ra at the time of 3 micrometers or less, and it turns out especially by Ra that the effectiveness is remarkable at th time of 1.5 micrometers or less so that clearly from drawing 1 . if this makes surface roughness small -- a titanium material front face -- an outline -- it becomes smooth and a particle is considered that it is hard coming to be caug physically and adhesion of a particle decreases.
[0017] On the other hand, the corrosion resistance which was excellent in titanium material originates in demonstrating the substrate protection nature in which the oxide film (formed with the gestalt of TiO, Ti 2O3, TiO2, etc.) which exists in a front face was excellent in various environments. It is thought that it is excellent the more the more the substrate protection nature by the oxide film of such titanium material has the large thickness an oxide film. Therefore, when carrying out thickness of the oxide film which exists in the front face of titanium material to the factor of the above (b) beyond a certain value, I thought that the minute amount elution of titanium

could be controlled.

[0018] Then, this invention persons investigated about oxide film thickness and the relation of a discoloration degree. The titanium material which changed various surface oxide-film thickness is put in in a chamber, and the oxide-film thickness when spraying the water which melted SOx and about 100 ppm of NOx in these front faces respectively for 48 hours, and the relation of a discoloration degree are shown in drawing 2 . At this time, adjustment of oxide-film thickness was adjusted after acid washing by the storage time amount or atmospheric-a oxidation treatment when keeping titanium material indoors. Moreover, viewing performed evaluation of discoloration, it divided into the group of 11 with extent of discoloration, what has the most intense discoloration was considered as the rank "0", and what has the fewest discoloration was evaluated as a rank "10." When the thickness of an oxide film is 20A or more so that clearly from this result, discoloration is mitigated, and also especially in this, thickness is a thing 40A or more, and it turns out that the discoloration mitigation effectiveness large.

[0019] In addition, if oxide-film thickness is carried out beyond a certain value, it is inapplicable to the titanium material as which a titanium material front face will be colored and such coloring is not required, but since it wil not become a coloring coat if the thickness of the oxide film is 100A or less, it does not produce such un-arrangin However, it is if it is in the inconvenient titanium material which is not even if it colors. Of course, it is not necessary to take such a point into consideration. Moreover, in the above-mentioned investigation, the storage tim amount of titanium material can adjust oxide-film thickness, because the titanium material front face used as activity reacts with the oxygen in atmospheric air, and moisture and the oxide film is formed of acid washing. Although an oxide film may grow to about dozens-100A depending on an environment at this time, since there is also no contamination of fines in a coat generation process in inside-of-a-house storage and there is also no adhesion of a sulfuric acid, a nitric acid, etc., unlike the case of the outdoors, it is hard to produce the discoloratio by coat growth (however, if it exceeds 100A, it will color).

[0020] And when controlling surface roughness and oxide film thickness based on the above-mentioned examination result to become a suitable value, a header and this invention were completed for much more dirt prevention effectiveness with the passage of time being acquired according to these synergistic effects. namely, - while the surface roughness of titanium is set as a suitable value and said suspension component carried out stop being able to adhere to an oxide film front face easily -- in addition -- and it is prevented that the oxide film whic involved in the gas constituents from which this oxide film will demonstrate the function as a barrier layer, and w cause discoloration under a pure ambient atmosphere if the oxide film of suitable surface roughness is formed beforehand is formed after that.

[0021] By the way, although not limited especially about the method of manufacturing the titanium material of th invention, it can manufacture, adjusting surface roughness and oxide film thickness, for example by the followin approaches.

[0022] Adjustment of the surface roughness of titanium material can be performed by adjusting the surface roughness of a reduction roll, and rolling load and a rate, if it is used with the rolling skin. Acid washing is carrie out after rolling, and if it is the titanium material used with the acid-washing skin, adjustment of surface roughne can be performed by adjusting the component of acid-washing liquid, a presentation, temperature time amount, e Moreover, adjustment of surface roughness can also carry out skin pass rolling and a dull roll pressure total after acid washing or rolling. That is, the order of the granularity of a base is several micrometers, since the order of th thickness of an oxide film is several 10 - 100A of numbers, it is the thickness of an oxide film and roughness doe not change. Therefore, if the surface roughness of base titanium material is adjusted, the surface roughness will b reflected and it will become the surface roughness after oxide film formation.

[0023] If adjustment of oxide-film thickness is kept on the other hand in the environment where the atmospheric polluted [industrial area / a direct rainstorm like indoor,] in the titanium material after acid washing when it was the case where it was used with the acid-washing skin cannot be touched (in short) That what is necessary is just keep it in places other than the environment leading to the discoloration described so far, although there is a difference by the storage area, time amount, etc., it reacts with the oxygen in atmospheric air, and moisture, and a oxide film grows from several 10A automatically to about 100A (it is thought that the oxide film thickness immediately after acid washing is close to 0). Moreover, although vacuum annealing is usually performed after rolling when using it with the rolling skin, a several angstroms - about 10A oxide film will usually exist also afte vacuum annealing. And since it is dependent on vacuum-annealing conditions (a degree of vacuum, temperature, time amount, etc.), oxide film thickness is adjusted on these conditions, or it is indoors like acid-washing materia after vacuum annealing, period storage is carried out, and you may make it the amount of this oxide film grow up

an oxide film.
[0024] As an approach of forming an oxide film in a titanium material front face compulsorily and efficiently, th are an oxidizing method by heat treatment and an anodizing method which passes the electrical and electric equipment to titanium in a solution, and forms an oxide film. Although usually used for coloring on the front fac of titanium, since these approaches can perform control of oxide-film thickness simply according to these processings, they become controllable [oxide-film thickness] positively according to the surface quality require of titanium material. For example, what is necessary is to control processing conditions and just to form an oxide film 100A or less, since a coloring coat will not be formed if oxide film thickness is 100A or less like the above when not coloring titanium material but using it with a base.
[0025] On the other hand, a coloring matter may be called for depending on an application. In this case, by cente line average granularity Ra, if surface roughness grows up oxide-film thickness until it becomes the color tone demanded by performing oxidation treatment or anodizing by heat treatment using titanium material (3 microme or less or 1.5 micrometers or less), it can obtain the titanium material excellent in dirt-proof nature.
[0026] In addition, although this invention has prescribed the thickness of the oxide film, this value can be calculated by the depth direction component analysis of the titanic-acid ghost coat by Auger electron spectroscop (the AES method). That is, the spatter time amount taken for an oxygen density to decrease to maximum density and the middle concentration of base density can be multiplied by it and asked for a sputtering rate. The sputterin rate at this time is SiO2 at the spatter conditions at the time of measurement. The rate when carrying out a spatter used. Drawing 3 shows typically how to ask for oxide film thickness from the depth direction component-analysi result of the titanic-acid ghost coat by the AES method.
[0027] Although an example explains this invention to a detail further below, the following example is not the th of the property which limits this invention, and each thing marked and done to before and the after-mentioned meaning for a design change is included in the technical range of this invention.
[0028]
[Example] The pure titanium material adjusted to various surface roughness (surface roughness after oxide-film formation) and various oxide-film thickness is put in in a chamber, and it is Fe, C, NaCl, and SiO2 to these samp front faces. Microscopic powder and the water which melted SOx and about 100 ppm of NOx, respectively were sprinkled for one month, and the surface discoloration situation was investigated. The ambient atmosphere at this time was made into the 70-80-degree C elevated temperature and the environment of 99% of humidity which discoloration tends [very] to produce as humid. that is, it is a kind of discoloration accelerated test, and this trial markedly boiled compared with an outdoor operating environment, it is a severe environment and can be generat in anticipated use to discoloration of extent which must have been produced.
[0029] As a sample, although the thing which carried out acid washing, or (1) atmospheric-air annealing -> salt immersion ->(2) vacuum annealing of the 1 sort of JIS commercially-pure-titanium cold-rolled material was carr out, adjustment of surface roughness was performed using either by rolling out using the reduction roll with whic control (a presentation, time amount, and temperature are adjusted) of acid-washing conditions differs from surfa roughness. Moreover, adjustment of the thickness of an oxide film kept the sample after acid washing or vacuum annealing for one week to one year to indoor [of various environments (temperature differs from humidity)], an was carried out by atmospheric-air oxidation treatment or anodizing. About the obtained titanium material, the discoloration degree (it is hereafter called "dirt-proof nature") was evaluated by viewing. the result -- the manufacture hysteresis of titanium material, and a front face -- it is shown in the following table 1 with descriptio (surface roughness, oxide film thickness, existence of coloring). The valuation basis of **** dirt nature is as follows.
[0030] [The valuation basis of dirt-proof nature]
O : pole small deer discoloration has not arisen as compared with the sample before a trial.
O : although it has discolored a little as compared with the sample before a trial, the degree is still small.
**: It is the average discoloration level of the titanium material currently used outdoors. O Although discoloratio is produced rather than the thing of O, it is not a thing to the extent that a fine sight is spoiled.
x: It has discolored remarkably and there is a possibility of spoiling a fine sight.
[0031]
[Table 1]

h g cg b eb cg e e

試料 No.	製造履歴	表面粗度Ra (μm)	酸化皮膜厚さ (Å)	着色の有無	耐汚れ性	備考
1	圧延→焼鈍→酸洗→屋内保管	0．5	20	無着色材	○	実施例
2	〃	1．2	35	〃	○	〃
3	〃	1．5	35	〃	○	〃
4	〃	2．0	20	〃	○	〃
5	〃	3．0	50	〃	○	〃
6	〃	0．5	80	〃	◎	〃
7	〃	1．2	40	〃	◎	〃
8	〃	1．5	60	〃	◎	〃
9	圧延→真空焼鈍→室内保管	0．6	30	無着色材	○	実施例
10	〃	1．5	25	〃	○	〃
11	〃	2．5	35	〃	○	〃
12	〃	3．0	45	〃	○	〃
13	〃	1．5	45	〃	◎	〃
14	〃	1．2	60	〃	◎	〃
15	圧延→焼鈍→酸洗→大気酸化	0．5	55	無着色材	◎	実施例
16	〃	1．5	60	〃	◎	〃
17	〃	1．2	80	〃	○	〃
18	〃	3．0	90	〃	○	〃
19	〃	1．5	240	着色材	◎	〃
20	〃	3．0	400	〃	○	〃
21	圧延→焼鈍→酸洗→陽極酸化	0．3	45	無着色材	◎	実施例
22	〃	1．4	60	〃	◎	〃
23	〃	3．0	80	〃	○	〃
24	〃	1．4	300	着色材	◎	〃
25	〃	3．0	600	〃	○	〃
26	圧延→焼鈍→酸洗→屋内保管	0．5	10	無着色材	△	比較例
27	〃	3．5	20	〃	△	〃
28	〃	2．5	10	〃	△	〃
29	〃	3．5	10	〃	×	〃
30	圧延→真空焼鈍→室内保管	3．5	15	無着色材	×	比較例
31	圧延→焼鈍→酸洗→大気酸化	4．0	100	着色材	△	比較例
32	圧延→焼鈍→酸洗→陽極酸化	3．5	150	着色材	△	比較例

[0032] From Table 1, it can consider as follows. First, although after [vacuum annealing] inside-of-a-house storage is carried out and an oxide film is formed, since surface roughness is 3 micrometers or less in center line average-of-roughness-height Ra and oxide film thickness is 20A or more, as for the thing of sample No.1-14, all known by acid washing or excelling in dirt-proof nature. Among these, especially the thing of sample No.6-8, an 13 and 14 shows the dirt-proof nature which was excellent especially since surface roughness was 1.5 micromete or less in center line average-of-roughness-height Ra and oxide film thickness was 40A or more.

[0033] Although atmospheric-air oxidation or anodizing is carried out after acid washing and an oxide film is formed compulsorily, since surface average-of-roughness-height Ra is 3 micrometers or less and oxide film thickness is 20A or more, as for the thing of sample No.15-25, all are known by excelling in dirt-proof nature. Among these, especially the thing of sample No.15, and 16, 19, 21, 22 and 24 shows the dirt-proof nature which was excellent especially since surface roughness was 1.5 micrometers or less in center line average-of-roughness height Ra and oxide film thickness was 40A or more.

[0034] moreover, sample No. -- although the thing of 20 and 25 formed the thick oxide film (400A and 600A), since surface roughness was 3 micrometers of an upper limit in center line average-of-roughness-height Ra, it did not become evaluation of O. It can be judged that it is important when controlling both surface roughness and ox film thickness in the predetermined range makes dirt-proof nature good from this.

[0035] On the other hand, since either surface roughness or oxide film thickness had separated from the range specified by this invention, discoloration has arisen and the thing of sample No.26-28, and 31 and 32 became evaluation of **. moreover, sample No. -- the thing of 29 and 30 -- both surface roughness and oxide film thickn -- although -- since it had separated from the range specified by this invention, it had discolored remarkably and became evaluation of x.

[0036] In addition, the thing of sample No.15-18, and 21-23 was not colored because the thickness of the formed oxide film was 100A or less, and if it becomes beyond this value, it will become a coloring coat by the interferen action of light. Moreover, although only pure titanium material is used in the above-mentioned example, it is not shown that this invention can apply this only to pure titanium. That is, since it is obtained because the effectivene of this invention controls surface roughness and scaling coat thickness in the proper range, also when using titanium-alloy material, it is needless to say [this invention] that it is applicable.

h g cg b eb cg e e

[0037]
[Effect of the Invention] As stated above, according to this invention, the secular dirt by an outdoor use etc. could be prevented or mitigated, and the titanium or the titanium-alloy material which continues at a long period of tim and discoloration does not generate was able to be obtained. Moreover, roofing, a wallplate, and when it is furthe used as materials, such as monument material, the titanium or the titanium-alloy material obtained in this way ca attain a maintenance free, and is very useful.

[Translation done.]